which sufficient ammonium hydroxide is added to give a decided odor. The crystals are washed with ether. When dry the purification is completed by a recrystallization from hot benzene; yield, 2 g.; white microscopic needles. The compound shows a slight shrinkage at about 139° and melts at 142–143°. It is tasteless and odorless. Concentrated sulfuric acid gives a colorless solution which upon heating becomes a faint straw color.

Anal. Calcd. for $C_9H_{12}O_2N_2$: C, 60.0; H, 6.66; N, 15.56. Found: C, 60.10; H, 6.72; N, 15.64.

The compound is soluble in hot water, ethanol, amyl alcohol and hot benzene. It is very slightly soluble in ether.

CONTRIBUTION FROM THE
CHEMICAL LABORATORY OF THE
UNIVERSITY OF ARKANSAS
FAYETTEVILLE, ARKANSAS
E. WERTHEIM

RECEIVED AUGUST 23, 1930
PUBLISHED OCTOBER 6, 1930

COMMUNICATIONS TO THE EDITOR

DR. C. S. HUDSON'S VIEWS ON THE RELATIONSHIP OF STRUCTURE TO THE OPTICAL ROTATIONS OF SUGARS

Sir:

Dr. C. S. Hudson has not utilized the means which were open to him to test the validity of his views by direct chemical experiments. The basis on which he develops his argument is the presumed existence, which his statistical methods enable him to detect, of a new form of mannose (calculated $[\alpha]_D$ +77°) in derivatives of 4-glucosido-mannose, obtainable from cellobiose through cellobial. If this foundation for his scheme fails, then the entire superstructure of rival formulas which he has raised upon it must collapse.

A survey of his two recent papers [THIS JOURNAL, **52**, 1680, 1707 (1930)] has led me to select for this critical test an experimental method which he has tacitly approved: he has accepted and utilized the observation of Fischer and Armstrong that β-methylmaltoside gives rise by enzyme hydrolysis to β-methylglucoside without ring change. Implicit in Dr. Hudson's scheme, therefore, is the expectation that 4-glucosido-α-methylmannoside will yield by enzyme cleavage his hypothetical α-methylmannoside ($[\alpha]_D$ +125°), inasmuch as this is the glycoside of the unknown form of mannose to which he has assigned the 1,5-ring.

With my colleague Dr. E. L. Hirst and other co-workers (R. J. W. Reynolds, H. R. L. Streight, H. A. Thomas, J. I. Webb and Miss M. Plant) I have prepared and investigated the chemical behavior of both 4-glucosido-α-methylmannoside and 4-galactosido-α-methylmannoside to which the 1,4-ring cannot apply since the 4-position in the mannose residue is occupied by the biose link. Both these substances are hydrolyzed by *emulsin* and yield the ordinary known form of α-methylmannoside ($[\alpha]_D$ +79°) which is the pyranoside (1,5-ring).

The above biosides are prepared in the same way as the bioses, namely, from cellobial and lactal by the action of perbenzoic acid, but in the presence of methyl alcohol instead of water. The same 4-glucosido-α-methylmannoside has also been obtained from acetobromo-glucosidomannose.

Had Dr. Hudson tried these experiments it is difficult to see how he could have committed himself to speculations that are at variance with this and with much more chemical evidence which is on record. Moreover, the rotations of these biosides and of the corresponding bioses are widely divergent from those required by his system of classification based on epimeric differences with cellobiosides and lactosides and the free sugars. The "principle of optical superposition" cannot be applied uniformly throughout the sugar group. The results now summarized are in complete agreement with the sugar formulas we have established by methylation studies, lactone formation and degradation, and by a comparison of the reaction velocities of glycosides under hydrolysis, and by other direct chemical methods.

THE UNIVERSITY OF BIRMINGHAM
EDGBASTON, ENGLAND
W. N. HAWORTH

RECEIVED JULY 30, 1930
PUBLISHED OCTOBER 6, 1930

POSSIBLE USE OF THE POULSEN ARC AS A MEANS OF DETECTING TRACES OF IMPURITIES IN METALS

Sir:

It has been shown by one of us in conjunction with E. Z. Stowell[1] that an atmosphere of hydrogen and usually cathode materials which are elements of even atomic number are necessary to produce radio frequency oscillations in the Poulsen Arc.

In the non-oscillating or ordinary direct current arc in hydrogen, the spectra of copper and sodium were revealed when these elements were used as cathodes. Upon connecting the oscillating circuit, the spectra of copper or sodium were either entirely suppressed, or appeared only faintly. Simultaneously the spectra of elements such as zinc, titanium and aluminum which will support oscillation, and which were present in small amount as impurities in the cathode metal, either appeared or if previously present were greatly accentuated.

The spectrum of H_B showed the presence of more atomic hydrogen in the oscillating than in the non-oscillating arc. Chemical analysis of the electrolytic copper showed titanium and aluminum present as 0.005 and 0.0045%, respectively.

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[1] Stowell and Redeker, *Phys. Rev.*, **34**, 978 (1929).

When using an ammonia atmosphere and a tip of gold brazed onto a water-cooled copper cathode, the oscillating arc completely suppressed the spectra of these metals, and intensified the 3361–3372 Å. line of the titanium impurity in the copper. The above phenomena suggested the use of the Poulsen Arc as a means of detecting small traces of impurities of even atomic number in such metals as copper, gold and silver.

A quantitative analytical method involving these phenomena is now being worked out in this Laboratory.

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY
STANFORD UNIVERSITY, CALIFORNIA
HARRY E. REDEKER
PHILIP A. LEIGHTON

RECEIVED SEPTEMBER 2, 1930
PUBLISHED OCTOBER 6, 1930

COAGULATION OF PURE FERRIC HYDROXIDE SOLS

Sir:

In a recent article Judd and Sorum [THIS JOURNAL, **52**, 2598 (1930)] have stated that with highly purified sols of ferric hydroxide, which are practically free from chloride ions, the amount of univalent coagulating ion decreases as the concentration of the sol increases.

In several publications [*J. Phys. Chem.*, **26**, 701 (1922); **28**, 313 (1924); **29**, 435, 659 (1925); *Kolloid.-Z.*, **34**, 262 (1924); **36**, 129 (1925)] from these Laboratories we have shown that ordinarily purified sols of ferric hydroxide require larger amounts of univalent electrolytes for coagulation when the concentration of the sol is increased. In a recent communication Dhar and Gore [*J. Indian Chem. Soc.*, **6**, 31 (1929)] have shown that even highly purified sols of ferric hydroxide containing a very small amounts of chloride ion follow the general rule that the greater the concentration of the sol, the greater is the amount of electrolyte necessary for coagulation irrespective of the valency of the coagulating ion. It appears, therefore, that the results of Judd and Sorum are not in agreement with previous work and need confirmation.

CHEMICAL LABORATORY
ALLAHABAD UNIVERSITY
ALLAHABAD, INDIA
N. R. DHAR

RECEIVED SEPTEMBER 6, 1930
PUBLISHED OCTOBER 6, 1930

A CONTINUOUS (OR BAND) FLUORESCENCE EMISSION SPECTRUM WHICH ACCOMPANIES A CHANGE OF COLOR

Sir:

An interesting phenomenon has been observed in a study of the Raman effect with a number of liquids listed later. A continuous (or band) emission spectrum (Fig. 1) has been found to appear on the plate in each case in which the colorless liquid becomes colored, and not to appear if there is no color change. The incident radiation of the mercury arc light appears to excite the molecules of the substance, and a part of the energy of excitation is released as a fluorescence radiation. A few of the details of this work are given below.

The Raman effect has been observed for a number of bromides: normal butyl bromide, secondary butyl bromide, isobutyl bromide, tertiary butyl bromide, normal propyl bromide, isopropyl bromide, normal amyl bromide and isoamyl bromide. The liquids were purified by distillation.

In addition to the lines of modified wave length, a continuous spectrum, which lies within the limits $\lambda = 4000$ Å. and $\lambda = 5800$ Å., was obtained with each liquid. The continuous spectrum was always accompanied by the appearance of a yellow color in the liquid. Usually an exposure of forty-eight hours sufficed for the production of the continuous spectrum; this, however, was not the case with *n*-propyl bromide, *n*-butyl bromide and secondary butyl bromide, since none of these showed either a continuous spectrum or a discoloration after being exposed to the mercury arc for forty-eight hours. If the time of exposure was extended to seventy-two hours or more, the continuous spectrum and the color change were observed for each of these liquids. In all cases where the exposure was long enough to give an intense continuous spectrum, the latter contained two regions of maximum intensity, one lying between the mercury lines at $\lambda = 4358$ Å. and $\lambda = 4916$ Å., and the other between the lines at $\lambda = 5460$ Å. and $\lambda = 5769$ Å.

Methyl and ethyl alcohols saturated with ammonia were studied for Raman spectra. The solutions were exposed to the mercury arc for ten to twelve hours. Methyl alcohol saturated with ammonia gave a continuous spectrum which was similar to that of the bromides in character and in position; the solution turned yellow during the exposure. Ethyl alcohol saturated with ammonia did not give a continuous spectrum or a color change. Neither of these two accompanying phenomena was observed in the case of the pure alcohols.

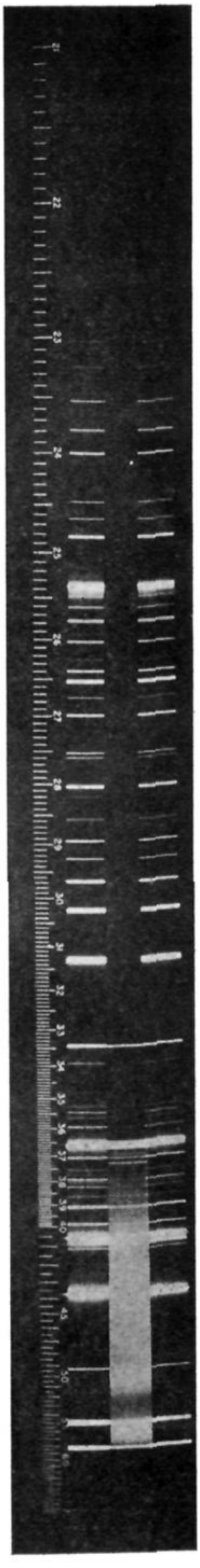

Fig. 1.—In the middle is the continuous fluorescence spectrum and the Raman spectrum of an alkyl bromide. The mercury comparison spectrum is shown above and below.

An attempt was made to ascertain whether the exclusion of oxygen would affect the color change and the continuous spectrum. A brisk stream of nitrogen was bubbled through isoamyl bromide for forty-five minutes prior to exposure and the Raman tube was closed by means of a stopcock; no diminution of the intensity of the continuous spectrum or of the color, was found.

KENT CHEMICAL LABORATORY
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CHICAGO, ILLINOIS

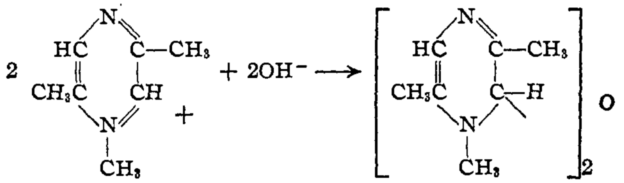
RECEIVED SEPTEMBER 8, 1930
PUBLISHED OCTOBER 6, 1930

WILLIAM D. HARKINS
H. E. BOWERS

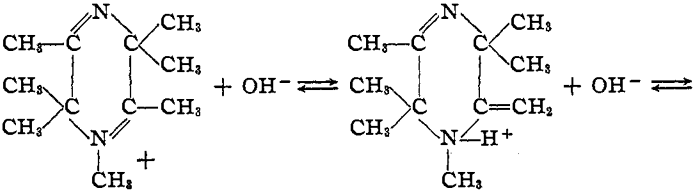
THE BASE FROM 2,5-DIMETHYLPYRAZINE-METHYL IODIDE

Sir:

Recently Principalle[1] has reported unsuccessful attempts to isolate the base liberated from 2,5-dimethylpyrazine-methyl iodide. In connection with some work on pseudo bases, part of which has already been submitted for publication, the author has studied the action of alkali on this salt. Although the base isolated could not be obtained pure and gave analyses varying from C, 53.2; H, 6.94, to C, 49.5; H, 6.63, a kinetic study of the reaction using a conductimetric method has made it seem probable that the net reaction taking place is



The salts 1,2,2,5,5-pentamethyl-2,5-dihydropyrazinium iodide and 1,2,-2,3,5,5,6-heptamethyl-2,5-dihydropyrazinium iodide have also been prepared and their behavior with aqueous alkali studied. From these two salts the bases isolated were, respectively, 1,2,2,5,5-pentamethyl-6-hydroxy-1,2,5,6-tetrahydropyrazine (m. p. 110°) and 1,2,2,3,5,5-hexamethyl-6-methylene-1,2,5,6-tetrahydropyrazine (b. p. (6.5 mm.) 78°). Certain evidence has been obtained to show that the latter base was formed by an enolic change



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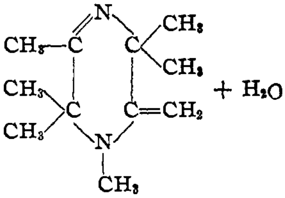
[1] Princivalle, *Gazz. chim. ital.*, **60**, 298–301 (1930); *C. A.*, **24**, 3792 (1930).



It is believed that the reduced conjugation in the ring is the cause of this reaction, which does not occur in the case of 1,2,5-trimethylpyrazinium iodide. It is to be noted that the same reduced conjugation occurs in 1,2,5-trimethyl-6-keto-1,6-dihydropyrazine-methyl iodide, which by the action of alkali yields 1,2,4-trimethyl-5-methylene-6-keto-1,6,4,5-tetrahydropyrazine.[2]

It seems likely, in view of the above results, that the last compound is yielded by an enolic change similar to that already mentioned and that the reduced conjugation is the important factor in its production.

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John G. Aston

Received September 11, 1930
Published October 6, 1930

PRELIMINARY NOTE RELATING TO STUDIES ON KRYPTON AND XENON

Sir:

A research project having to do with the purification and properties of krypton and xenon has been in progress during the past four years. Some rather novel results have been obtained to which the authors desire to call attention at this time since the work has been interrupted on account of unavoidable delays attendant upon moving into a new building. A more complete report will follow at an early date.

Liquid air residues, mainly oxygen, were treated by cooled charcoal in a manner which concentrated the krypton and xenon considerably. The excess oxygen and other reactive gases were removed by suitable reagents and the remaining inert gases were separated by repeated fractional distillation. Finally about 70 cc. of krypton and 30 cc. of xenon were obtained in a condition of very high purity.

One of the first things investigated was the melting point. Krypton gave an exceedingly sharp melting point at −156.6° with a corresponding vapor pressure of 558 mm. Note a difference of about 12° from the −169° previously accepted as the melting point.

Xenon was harder to deal with in that it failed to give the sharp melting point that had been noted with krypton. Its behavior indicated the possibility of a transition point quite close to the melting point. The

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[2] Gastaldi and Princivalle, *Gazz. chim. ital.*, 59, 791 (1929); Princivalle, *ibid.*, 60, 296, 298 (1930).

melting point may be given, however, as −111.5 ± 0.5° with a corresponding vapor pressure of 600 ± 20 mm. The accepted value for the xenon melting point is approximately −140°.

The processes of purification were checked by frequent density determinations and the densities of the best samples of krypton and xenon were rather carefully determined. The method employed was to collect a sample of the gas at a known temperature and pressure in a calibrated bulb, which was then weighed against a counterpoised bulb.

Density determinations made in connection with the fractionation work seem to indicate that the present accepted densities for krypton and xenon are too low. The value found for the heaviest krypton fraction was 3.733 g./l. and that for the heaviest xenon fraction 5.887 g./l. These figures would correspond, respectively, to atomic weights of 83.6 and 131.4 if Watson's [*J. Chem. Soc.*, **97**, 833 (1910)] corrections are employed. No effort has yet been made to make final density determinations and these will be reported later.

Much of the work of extraction and purification followed the lines indicated by earlier investigators, but a number of new methods were used which will be reported in the more complete paper.

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R. B. Moore

Received September 13, 1930
Published October 6, 1930

NEW BOOKS

Optical Activity and High Temperature Measurements. By F. M. Jaeger. McGraw-Hill Book Company, Inc., 370 Seventh Avenue, New York, 1930. 450 pp. 137 figs. 15.5 × 23.5 cm. Price, $4.00.

This volume contains the lectures delivered at Cornell University by Professor F. M. Jaeger during the second semester of 1928–1929 under the George Fisher Baker Non-Resident Lectureship in Chemistry. There are three series of the lectures. The first deals with the spatial arrangement of atomic systems and optical activity; the second with the methods, results and problems of precise measurements at high temperatures; the third with the constitution and structure of the ultramarines. Taken as a whole the lectures furnish a systematic presentation of investigations carried out by Professor Jaeger and his co-workers at the chemical laboratory of the University of Gröningen.

The first lectures of the first series cover the principles of symmetry as applied to atomic systems, discussing the work of Pasteur, van't Hoff and Le Bel. The remaining lectures of this series are concerned chiefly with the optical activity of complex salts, many of them essentially inorganic. These latter lectures are of particular interest as demonstrating the wide-